Deuterium NMR Study of the Solid-Solid Phase Transition in Phenethylammonium Bromide

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Z. Naturforsch. **46a,** 691–696 (1991); received March 30, 1991

Using ^2H NMR, the dynamics of the cation in phenethylammonium bromide were studied in the two solid phases. Line shape and spin-lattice relaxation rate studies of the ammonium headgroups and the adajacent methylene groups indicate the onset of alkyl-chain motion prior to the first order phase transition. In the low-temperature phase the line shape and the spin-lattice relaxation rates of the $-ND_3$ groups are consistent with C_3 jumps and an activation energy of 54 ± 4 kJ mol^{-1}. However, in the high-temperature phase the spin-lattice relaxation studies indicate the presence of small-angle diffusion of the $-ND_3$ groups around the C_3 symmetry axis. In this phase the $-CD_2-$ groups show line shapes typical of large-amplitude two-site jumps occurring at a rate $> 10^7$ s^{-1}. In the low-temperature phase, at temperatures below 295 K, the $-CD_2-$ ^2H NMR line shapes indicate that the C–D bonds are essentially static.

Key words: ^2H NMR, Phase transition, Relaxation, Molecular jumps.

1. Introduction

At atmospheric pressure, phenethylammonium bromide (PENBr), Fig. 1, is known to exist in two crystalline forms [1]:

$$\text{Solid II} \leftarrow \left\{ \begin{matrix} 347\ \text{K} \\ \Delta S = 2.31\ \text{R} \end{matrix} \right\} \rightarrow \text{Solid I}\,.$$

Also the crystal structure of solid II is known at room temperature [2]. The compound forms a chain structure which has a bilayer type of symmetry. The crystal structure consists of a sawtooth layer of bromide ions which are hydrogen bonded with the ammonium headgroups in such a way that the phenalkyl residues remain perpendicular to the long axis of the sawtooth layer. Coefficients of thermal motion increase in the order: Br, N, C of the alkyl chain, C of the phenyl ring.

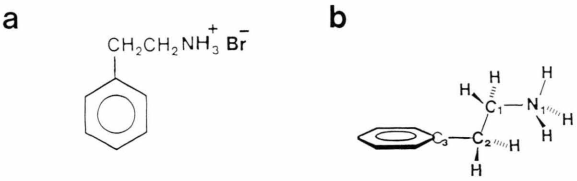

Fig. 1. a) Representation of phenethylammonium bromide. b) Conformation of the ethylammonium fragment of PENBr with respect to the phenyl-ring plane (Solid II phase at 293 K) [2]. The C_1–C_2–C_3 plane is twisted by approximately 75° (105°) from the phenyl-ring plane. The N_1–C_1–C_2–C_3 nuclei lie in an approximate all-trans arrangement.

Although differential scanning calorimetry indicated a large entropy change at the first order phase transition [1], it is difficult to deduce microscopic or dynamic information from these measurements. In order to study the dynamics of the cations in the two solid phases, deuterium (^2H) NMR line shape and spin-lattice relaxation studies of powder samples were carried out at various temperatures. Using specifically deuterium labelled analogues, the dynamics of the ammonium headgroup, $-ND_3$, and the adjacent methylene group, $-CD_2-$, were studied and characterized separately.

The ^2H NMR relaxation studies of the ammonium headgroup indicate that the dominant relaxation mechanism in solid II consists of C_3 jumps while in solid I the major contribution to the spin-lattice relaxation comes from small-angle diffusion of the $-ND_3$ groups around their C_3 axes. Line shape studies of the $-CD_2-$ groups indicate large amplitude two-site jumps for these groups in the solid I phase. Our study also indicated that a considerable amount of motion of the $-CD_2-$ groups is already present in the solid II phase within 10–20 K below the transition temperature.

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2. Theory and Experimental Aspects

Frequency spectra of deuterium are dominated by the quadrupole interaction of the nuclear quadrupole moment with the surrounding electric field gradient (EFG) at the nucleus. This interaction is taken as a first order perturbation to the Zeeman interaction. The NMR frequency is given by [3]

$$\omega=\omega_0\pm\tfrac{3}{4}\pi^2\langle\chi^2\rangle^{\frac{1}{2}}(3\cos^2\theta-1-\eta\sin^2\theta\cos 2\phi)\,, \quad (1)$$

where ω_0 ,and χ represent the Larmor frequency and quadrupole coupling constant (QCC), respectively. The orientation of the EFG tensor with respect to the static magnetic field is given by the polar angles (θ, ϕ). The EFG asymmetry parameter, η, can be assumed to be approximately zero for the N–D and C–D bonds studied here [4]. Deuterium NMR powder spectra of samples containing static C–D or N–D bonds typically have a maximum total width of ~250 kHz. The effect of anisotropic motion on ^{2}H NMR line shapes and rate of spin-lattice relaxation has been discussed by several other authors [5–7]. For motions with a threefold or higher symmetry and jump rates larger than the QCC, the ^{2}H NMR line shape is axially symmetric and can be obtained from the static line shape through the addition theorem of spherical harmonics [6–8]. Motions with less than threefold symmetry result in the introduction of spectral asymmetry in the ^{2}H NMR line shape [5, 6]. In all cases where the molecular jump rate is of the order of magnitude of the QCC, the rate of reorientation of the molecule must be introduced explicitly in order to calculate the line shape [5]. In this so-called intermediate exchange region, the experimental spectra strongly depend on the experimental parameters.

The relaxation rate of Zeeman (R_{1Z}) and quadrupolar (R_{1Q}) order is given by

$$R_{1Z}=\tfrac{3}{4}\pi^2\langle\chi^2\rangle\,[J_1(\omega_0)+4J_2(2\omega_0)]\,, \quad (2)$$

$$R_{1Q}=\tfrac{3}{4}\pi^2\langle\chi^2\rangle\,[3J_1(\omega_0)]\,. \quad (3)$$

The spectral densities $J_m(m\omega_0)$ are determined by the statistics of the molecular reorientation. For pure C_3 jumps explicit expressions for R_{1Z} and R_{1Q} were previously calculated [9]. In Table 1 the ratios of R_{1Z} and R_{1Q} are given for two orientations in the powder pattern and for two motional regimes. Relaxation studies can be used to discriminate between the different reorientational models which result in identical line shapes. The anisotropy of the spin-lattice relaxation across the powder pattern is very sensitive to the statistics of the reorientation.

All ^{2}H NMR experiments were performed on a Bruker MSL 200 at 30.72 MHz, using 4.0–4.5 μs $\frac{\pi}{2}$ pulses. The line shapes were acquired with the solid echo pulse sequence: $\frac{\pi}{2}|_x-\tau-\frac{\pi}{2}|_y-\tau$ [10], with phase cycling. Zeeman splin-lattice relaxation rates were measured with the solid-echo sequence preceded by an inversion, π, pulse. The relaxation of quadrupolar order was measured with a modified Jeener-Broekaert pulse sequence [11]. Details of the deuteration of PENBr can be found elsewhere [9]. Deuterium NMR line shapes were simulated with a modified Fortran program obtained from Griffin and co-workers [12]. The simulations presented here do not include the correction for spectral distortions due to the finite pulse lengths [13].

3. Results and Discussion

Figure 2 shows the ^{2}H NMR line shape of the $-ND_3$ headgroups at 292 K in the solid II phase. The line shape was found to be dependent on echo delay,

Table 1. Ratios of Zeeman and quadrupole spin-lattice relaxation rates for the $\theta=90°$ and $\theta=0°$ orientations in the powder line shape and two motional regimes. Pure C_3 jumps are assumed.

	$R_{1Z}(\theta)/R_{1Q}(\theta)$	
	$\omega_0\tau_{C_3}\ll 1$	$\omega_0\tau_{C_3}\gg 1$
$\theta=90°$	1.44	0.610
$\theta=\ 0°$	3.00	1.00

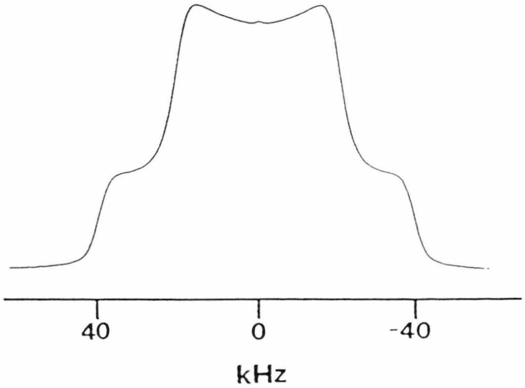

Fig. 2. ^{2}H line shape of the $-ND_3$ groups in PENBr at 292 K. The spectrum was acquired with a 40 μs echo delay.

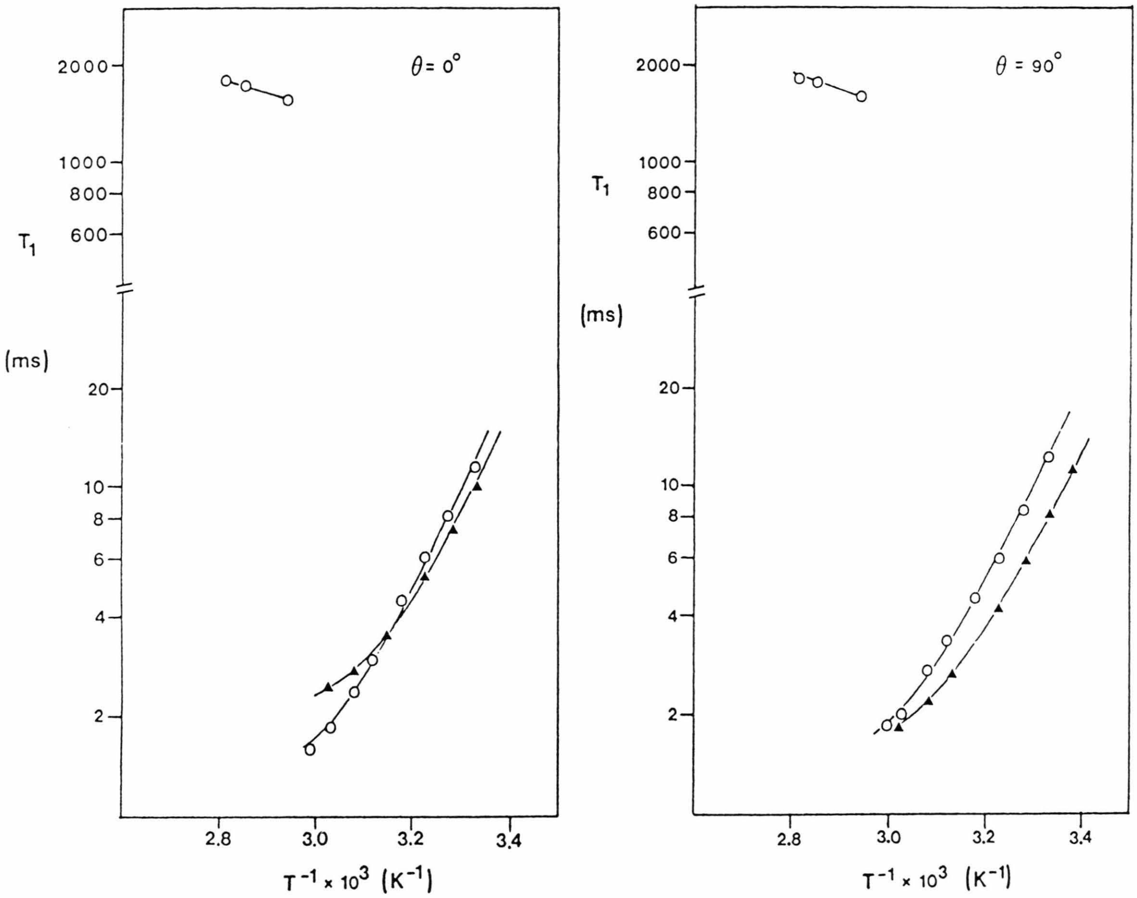

Fig. 3. ^2H Zeeman (○) and quadrupolar (△) spin-lattice relaxation times of the $-ND_3$ groups as a function of reciprocal temperature for the $\theta = 90°$ and $\theta = 0°$ orientations of the powder line shape (see text).

indicating that the rate of reorientation of the $-ND_3$ groups is in the intermediate exchange region, i.e., $\omega_Q \tau_{C_3} \simeq 1$. Eventually, with increasing temperature, the ^2H line shape becomes independent of the echo delay at $T > 320$ K, i.e., $\tau_{C_3} < 10^{-7}$ s. In addition to the thermally activated C_3 jumps another motion is present. For $T > 320$ K, a small temperature-dependent reduction of the quadrupolar splitting, which corresponds to the separation between the two $\theta = 90°$ orientations in the powder pattern, is observed. However, relaxation rate studies indicate (*vide infra*) that at those temperatures PENBr is still in the solid II phase. At temperatures just below the solid II–solid I phase transition, an axially symmetric $-ND_3$ ^2H NMR line shape with a quadrupolar splitting of 32 kHz was observed. This value is somewhat lower than the splitting of approximately 40 kHz expected for a typical N–D bond with a QCC of 165 kHz performing pure C_3 jumps and making an angle of 70.5° with the symmetry axis [14]. The $-ND_3$ ^2H NMR line shape did not change at the phase transition and still showed an axially symmetric powder pattern with a quadrupolar splitting of 32 kHz at 365 K.

Zeeman and quadrupolar relaxation studies were used to clarify this peculiar behaviour of the $-ND_3$ ^2H NMR line shape at the phase transition. In Fig. 3 Zeeman and quadrupolar relaxation times ($T_1 = R_1^{-1}$) are shown as functions of reciprocal temperature for the $\theta = 0°$ and $\theta = 90°$ orientations in the powder pattern. It should be noted that the $\theta = 90°$ orientation is actually an overlap of the $\theta = 90°$ and $\theta = 35.5°$ orientation of the two transitions within the $I = 1$ spin system. From Fig. 3 it is clear that at 292 K the $-ND_3$ reorientation is out of the extreme narrowing limit,

Table 2. Observed ratios of Zeeman and quadrupole spin-lattice relaxation rates for the $\theta=90^\circ$ and $\theta=0^\circ$ powder orientations of the $-ND_3$ groups in the Solid II phase of PENBr.

	$R_{1Z}(\theta)/R_{1Q}(\theta)$	
	$\omega_0\tau_{C_3} \ll 1$	$\omega_0\tau_{C_3} \gg 1$
$\theta=90^\circ$	–	0.65 ± 0.02
$\theta=0^\circ$	–	0.9 ± 0.1

i.e., $\omega_0\tau_{C_3} > 1$. The temperature dependence of the Zeeman and quadrupolar relaxation times indicates that C_3 jumps are the dominant relaxation mechanism. In Table 2 the ratios of the Zeeman and quadrupole relaxation rates are given for the two powder orientations. The values in Table 2 compare very well with the theoretical values in Table 1. A dramatic change in the Zeeman spin-lattice relaxation time of the $-ND_3$ groups was observed in the temperature region of 335–340 K. Just before the relaxation time minimum can be observed, the solid II–solid I phase transition occurs. The Zeeman relaxation time increases by approximately three orders of magnitude from $\simeq 1.8$ ms in solid II to $\simeq 1800$ ms in solid I. It was also observed that the anisotropy in the relaxation of Zeeman order disappeared in the high-temperature phase. In solid I both the $\theta=90^\circ$ and $\theta=0^\circ$ orientations of the powder line shape relaxed at the same rate. This cannot be explained with a C_3 jump model which predicts T_1 anisotropy, even for very fast jumps. However, small angle diffusion of the $-ND_3$ groups around their C_3 axis results in a vanishing T_1 anisotropy while the ^2H NMR line shape is identical to that for C_3 jumps [15]. It can thus be concluded that in solid I the $-ND_3$ groups of PENBr undergo small-angle diffusion. From Fig. 3 an activation energy of 57 ± 4 kJ mol^{-1} can be determined for the C_3 jumps in solid II from the Zeeman and quadrupolar relaxation times.

The difference of approximately 5 K in the transition temperature as obtained from differential scanning calorimetry and ^2H NMR studies is not well understood. However, PENBr was reported to exhibit an odd phase transition behaviour [1]. In order to avoid problems with hysteresis [1], all relaxation rates and line shapes were recorded as a function of increasing temperature. After heating to solid I temperatures the sample was first cooled for 30 minutes in liquid nitrogen before experiments in the solid II phase were repeated. All the ^2H NMR line shapes of the methylene groups were acquired with a 60 s recycle delay. This procedure resulted in reproducible results.

Deuterium NMR line shapes of the $-CD_2-$ groups are shown in Figure 4. At $T > 320$ K the ^2H line shape of the methylene groups is axially symmetric and has a quadrupolar splitting of ~ 112 kHz. This is somewhat lower than the typical value of 120 kHz obtained for static C–D bonds [16, 17]. For $T > 320$ K asymmetric ^2H NMR powder patterns were observed. The spectral asymmetry increases with increasing temperature. Since the line shapes were found to be independent of the solid echo delay, this reorientation must be in the fast motion limit, i.e., occurring with a rate greater than 10^7 s^{-1}. One component of the EFG tensor does not change with temperature. This indicates that the reorientation process is likely to be a two-site exchange process with equal populations. The effect of the two-site exchange on the EFG components is given by [14, 16, 17]

$$\begin{aligned} V_{xx}^{J} &= V_{zz} \sin^2 \alpha + V_{xx} \cos^2 \alpha, \\ V_{yy}^{J} &= V_{yy}, \\ V_{zz}^{J} &= V_{zz} \cos^2 \alpha + V_{xx} \sin^2 \alpha. \end{aligned} \tag{4}$$

The angle between the two equally populated sites is 2α, and the superscript J refers to the jump-averaged frame. With increasing temperature the spectral asymmetry increases since the jump angle increases. At $T = 320$ K a large asymmetry was observed (see Fig. 4) indicating the occurrence of a large amplitude two-site exchange process. Details of the spectral simulations are given in the legend of Figure 4. The ^2H NMR line shape of the $-CD_2-$ groups is temperature independent in the solid I phase and has a spectral asymmetry of $\eta = 1$. The simulations in Fig. 4 were performed with an effective QCC of 139 kHz. This value is approximately 20% smaller than the value expected for a rigid methylene group. The reduced QCC of 139 kHz results from motion (wobbles) of the ethylammonium chain. This motion is also responsible for the reduced splittings observed for the $-ND_3$ group (32 kHz vs. 40 kHz). Since the $-ND_3$ ^2H NMR line shape does not exhibit any spectral asymmetry, the reorientation of the C–D bonds must be such that these bonds move in a plane perpendicular to the C–N bond.

For the convenience of the interpretation of the methylene ^2H NMR results we will label the cation atoms in the following way: $\phi-C_2-C_1-N_1$ (see Figure 1b). The phenyl-ring ϕ, is bonded to the ethylammonium fragment through C_2-C_3 where C_3 de-

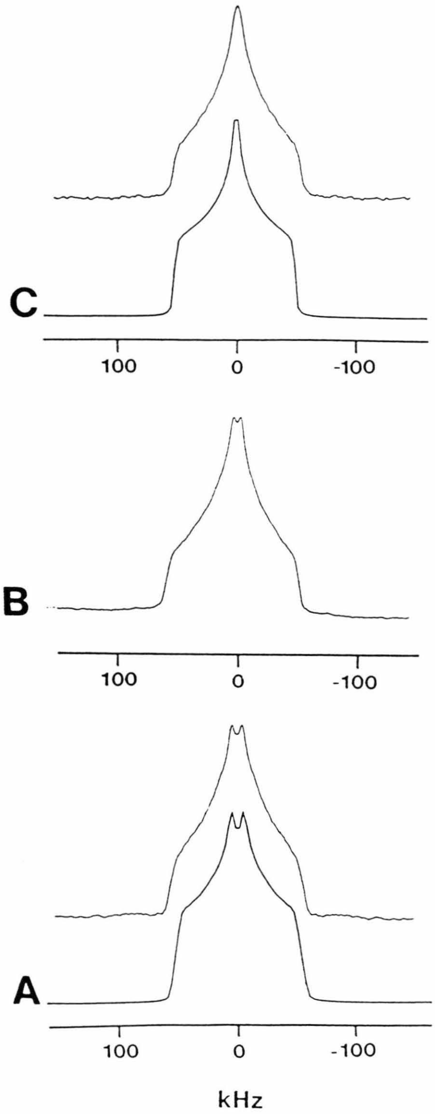

Fig. 4. ^{2}H line shape of the $-CD_2-$ groups at (a) 320 K, (b) 345 K and (c) 365 K. In all spectra the echo delay was set to 40 μs. Figure (a) was simulated with $\chi = 139$ kHz and $2\alpha = 67° \pm 1$ and (c) with $\chi = 139$ kHz and $2\alpha = 70° \pm 1$ (see text). The jumps are in the fast motion limit.

notes the ipso carbon of the phenyl-ring. X-ray crystallography data [2] of the Solid II phase indicate that the C_1 atom is not exactly perpendicular to the phenyl-ring plane (torsional angle ~105°) placing one of the C_2-H bonds almost parallel to the phenyl-ring plane. Rotational jumps of 120° about the C_2-C_3 bond axis move the C_1 atom to the opposite side of the phenyl-ring. Consider such a $\frac{2\pi}{3}$ jump in which the C_1-N_1 bond axis remains essentially parallel with the C_2-C_3 bond axis. Under these conditions the ^{2}H EFG of the $-ND_3$ group is not altered since the effective electric field gradient of the $-ND_3$ group is approximately parallel to the axis of rotation (see previous section). More interesting is the question of what happens to the ^{2}H EFG of the C_1 methylene deuterium nuclei. Inspection of molecular models together with the line shape simulations indicates that the C_1 bonded deuterium nuclei undergo two-site tetrahedral jumps over an angle of $180° - 70° \sim 109°$. Due to the symmetry of the quadrupolar Hamiltonian, jump angles of 2α and $180° - 2\alpha$ are equivalent. Thus, one can conclude that above the Solid II $\rightleftharpoons$ Solid I structural phase transition, rotational jumps of 120° about the C_2-C_3 bond axis may be responsible for the ^{2}H NMR line shapes observed for the C_1 methylene group (Figure 4). This model is consistent with the ^{2}H NMR results for both the $-C_1D_2-$ group and the $-N_1D_3$ group. We can not envision any other model consistent with the observations described here; however, we do not claim that the above model is unique [18]. In the Solid II phase of phenethylammonium bromide, we postulate that the motion of the C_1 carbon is restricted to large amplitude librational motions on one side of the phenyl-ring only.

4. Conclusions

Deuterium NMR line shape and spin-lattice relaxation studies of phenethylammonium bromide indicate the occurrence of alkyl-chain reorientation prior to the solid-solid phase transition. This motion consists of jumps between two equally populated sites and was also found to be present in the solid I phase. However, in the solid I phase the jumps occur with a larger jump angle. Since the $-ND_3$ ^{2}H NMR line shapes do not show any large change, it must be concluded that the motion of the methylene groups must occur in a plane perpendicular to the C–N axis. The motion could arise from rotational jumps around the C_2-C_3 axis.

The dynamics of the $-ND_3$ groups indicate a drastic change in the hydrogen bonding network upon the (first order) phase transition. In the solid I phase small-angle rotation of the $-ND_3$ groups around the C_1-N_1 axis occurs while in Solid II these groups perform discrete jumps between three sites. At the phase transition the ^{2}H NMR line shape of the $-ND_3$

groups does not change but the spin-lattice relaxation time changed by three orders of magnitude. The relaxation anisotropy present in Solid II vanished in the Solid I phase due to the onset of a diffusive motion. From the observed ^{2}H NMR line shapes of the $-C_1D_2-$ groups, the C_1-N_1 axis is considered to perform a large-amplitude motion around the C_2-C_3 axis of the molecule. Since the C_1-N_1 axis and the C_2-C_3 axis are approximately parallel, a rotation around the C_2-C_3 axis will not affect the $-ND_3$ deuterium line shape. Due to the tetrahedral two-site exchange observed at the $-C_1D_2-$ group in solid I, the rotational barrier for the $-ND_3$ three-site exchange in this phase must be low enough to allow small-angle diffusion.

In addition to the large-amplitude motions discussed above, an additional small-angle, symmetric, motion must occur at $T > 320$ K in order to explain the small reduction in the observed quadrupolar splitting of the $-ND_3$ line shape and the small reduction in the methylene QCC.

Acknowledgements

We would like to thank NSERC Canada for financial support, Dr. M. van Oort and Professor M. A. White for providing us with deuterated samples of phenethylammonium bromide. Also, we are grateful to Professor T. S. Cameron for the preliminary x-ray diffraction data on PENBr and Professor R. G. Griffin and co-workers for the line shape simulation program described in [12].

[1] M. Van Oort and M. A. White, Thermochim. Acta **139,** 205 (1989).
[2] S. Roe, O. Knop, and T. S. Cameron, unpublished results.
[3] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, Oxford 1961.
[4] C. I. Ratcliffe and J. A. Ripmeester, Can. J. Chem. **64,** 1348 (1986) and references therein.
[5] H. W. Spieß and H. Sillescu, J. Mag. Reson. **42,** 381 (1981).
[6] R. G. Griffin, K. Beshah, R. Ebelhäuser, T. S. Huang, E. T. Olejniczak, D. M. Rice, D. J. Siminovitch, and R. J. Wittebort, in: The Time Domain in Surfaces and Structural Dynamics (G. J. Long and F. Grandjeans, eds.), Kluwer Academic Publishers, Dordrecht 1988.
[7] D. A. Torchia and A. Szabo, J. Magn. Reson. **49,** 107 (1982).
[8] H. Margenau and G. M. Murphy, The Mathematical Principles of Physics and Chemistry, 2nd ed., D. van Nostrand Comp. Inc., Princeton N.J. 1967.
[9] M. L. H. Gruwel and R. E. Wasylishen, to be published.
[10] J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic, and T. P. Higgs, Chem. Phys. Lett. **42,** 390 (1976).
[11] J. Jeener and P. Broekaert, Phys. Rev. **157,** 232 (1967).
[12] R. J. Wittebort, E. T. Olejniczak, and R. G. Griffin, J. Chem. Phys. **86,** 5411 (1987).
[13] M. Bloom, J. H. Davis, and M. I. Valic, Can. J. Phys. **58,** 1510 (1980).
[14] M. L. H. Gruwel and R. E. Wasylishen, Z. Naturforsch. **45a,** 55 (1990).
[15] K. Beshah, E. T. Olejniczak, and R. G. Griffin, J. Phys. Chem. **86,** 4730 (1987).
[16] M. G. Taylor, E. C. Kelusky, I. C. P. Smith, H. L. Casal, and D. G. Cameron, J. Chem. Phys. **78,** 5108 (1983).
[17] E. C. Kelusky, I. C. P. Smith, C. A. Elliger, and D. G. Cameron, J. Amer. Chem. Soc. **106,** 2267 (1984).
[18] J. Hirschinger and A. D. English, J. Magn. Reson. **85,** 542 (1989).